

Optical atomic clocks with suppressed black body radiation shift.

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We study a wide range of neutral atoms and ions suitable for ultra-precise atomic optical clocks with naturally suppressed black body radiation shift of clock transition frequency. Calculations show that scalar polarizabilities of clock states cancel each other for at least one order of magnitude for considered systems. Results for calculations of frequencies, quadrupole moments of the states, clock transition amplitudes and natural widths of upper clock states are presented.

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I. INTRODUCTION

Atomic clocks are one of the most accurate tools ever designed that found application in many different modern technologies. Both optical lattice atomic clock [1] and ion clock [2] have demonstrated fractional accuracy at the level of few parts times 10^{-18} . There is a number of systematic shifts that one needs to overcome at this level of accuracy. One of the most challenging from technical point of view is the black body radiation (BBR) shift. The typical ways of removing this shift are either colling entire device to cryogenic temperatures [3] or building a

sophisticated thermal shields that allow to stabilize BBR shift, measure it and subtract later [1]. Both methods lead to considerable increase of complexity, size and price of the device.

It was suggested in [4–7] to use highly charged ions (HCI) for atomic clock purposes. Apart from many other advantages HCI have naturally suppressed BBR shift due to small values of scalar polarizabilities of clock states. Authors of [7] demonstrated that HCI with nf^2 two-electrons or two-holes configuration have optical transitions within the same configuration that allows to use them as an atomic clocks. In these systems there are ground and long-living first excited states with allowed electric quadrupole transition withing optical or infrared frequency range. It was pointed that the width of first excited state of the nf^{12} two-hole configuration was estimated to be an order of magnitude smaller than the one of two-electron nf^2 first excited state with the same transition frequency. An important conclusion of [7] is that clock transitions in HCI have many orders of magnitude larger quality factors than the ones found in modern atomic clocks. In the same time handling HCI is much more sophisticated task compared to working with low charged ions (LCI) and neutral atoms.

In this paper we investigate another way of reducing BBR shift in atomic clocks. The proposed systems are neutral atoms and low charged ions (LCI). We show that selected elements possess large quality factors and small BBR shifts. In the same time manipulations with them are accessible with developed experimental methods. We consider systems with suitable electric quadrupole clock transition within the same configuration. For LCI accurate numerical calculations show that for two-electron and two-hole configurations one can write the following inequality for transition matrix element values between ground and first excited states of the same configuration $A(nf^{12}) < A(nf^2) < A((n+1)d^8) < A((n+1)d^2) < A((n+2)p^4)$. Every next configuration in this sequence has about half an order of magnitude larger transition matrix element compared to the previous one. In the same time in our recent paper [8] we have investigated the $4f^{12}$ configuration for doubly ionized erbium together with the $4f^{12}6s^2$ of the neutral one. Since the $6s^2$ electrons form closed shell, energy level structure of these configurations is almost identical for both Er I and Er

TABLE I: BBR shift at room temperature of existing and prospective atomic clocks. If available, uncertainties are given in parenthesis.

Z	element	transition	$\beta_{BBR}, \times 10^{-18}$	reference
13	Al ⁺	$^1S_0 \rightarrow ^3P_0$	3.8(0.4)	[21]
38	Sr ⁺	$^2S_{1/2} \rightarrow ^2D_{5/2}$	670(250)	[22]
38	Sr	$^1S_0 \rightarrow ^3P_0$	5500(70)	[23]
40	Zr ²⁺	$^3F_2 \rightarrow ^3P_0$	9	this work
40	Zr	$^3F_2 \rightarrow ^3P_0$	621	this work
47	Ag	$^2S_{1/2} \rightarrow ^2D_{5/2}$	190	[24]
52	Te	$^3P_2 \rightarrow ^3P_0$	112	this work
53	I ⁺	$^3P_2 \rightarrow ^3P_0$	15	this work
54	Xe ²⁺	$^3P_2 \rightarrow ^3P_0$	4	this work
68	Er ²⁺	$^3H_6 \rightarrow ^3F_4$	<63	this work
68	Er	$^3H_6 \rightarrow ^3F_4$	<570	this work
69	Tm ³⁺	$^3H_6 \rightarrow ^3F_4$	<3	this work
70	Yb ⁺	$^2S_{1/2} \rightarrow ^2D_{3/2}$	580(30)	[25]
70	Yb ⁺	$^2S_{1/2} \rightarrow ^2F_{7/2}$	234(110)	[26]
70	Yb	$^1S_0 \rightarrow ^3P_0$	2400(250)	[23]
71	Lu ⁺	$^1S_0 \rightarrow ^3D_1$	54	this work
72	Hf	$^3F_2 \rightarrow ^3P_0$	855	this work
84	Po	$^3P_2 \rightarrow ^3P_0$	185	this work
90	Th	$^3F_2 \rightarrow ^3P_0$	303	this work
91	Pa ³⁺	$^3H_4 \rightarrow ^3F_2$	21	this work
91	Pa ³⁺	$^3F_2 \rightarrow ^3P_0$	20	this work

III. Clock transitions in both neutral and doubly ionized erbium have almost the same frequency that differs only by 46 cm^{-1} . The radiation widths of corresponding excited state in neutral erbium were only several times larger than the one of doubly ionized erbium. We anticipate the same inequality to hold for two-electron or two-hole neutral atoms with extra $(n+2)s^2$ electrons.

Important disadvantage of proposed elements is large value of total angular momentum J in one or both clock states. When $J \geq 1$ the atom or ion has a non-zero quadrupole momentum which couples to the electric field gradient. It can be especially important for optical lattice atomic clocks since the electric field gradient of trap laser can have relatively high values. In order to estimate this effect we perform calculations of quadrupole moments for considered systems.

II. SYSTEMATIC SHIFTS IN ATOMIC CLOCKS

A number of systematic shifts affect and limit the accuracy of atomic clocks. Among the main ones there are black body radiation shift (BBR), interaction of atomic quadrupole moments with gradients of electric field, micro and secular motion, Stark and Zeeman shifts, background-gas collisions, gravitational shift, etc. Some of these factors were discussed in [2, 13]. The most significant factors are BBR, quadrupole and Zeeman shifts. Zeeman shift and other effects due to influence of the external magnetic field on the clock transition were widely investigated (see for example [2, 11, 12]), well known methods are developed in order to minimize or cancel corresponding shifts. In the same time the black body radiation shift (BBR) remains the most significant obstacle on the way to more accurate and compact atomic clocks. As was mentioned in introduction for proposed elements quadrupole shift may also be essential and requires consideration.

A. Black Body Radiation shift

The BBR shift originates from perturbation of the clock states by the environment photon bath due to dynamic Stark shift. The magnitude of this shift is given by the following equation [23]

$$\frac{\Delta\omega}{\omega_0} \Big|_{\text{BBR}} \approx -\frac{2\pi^3\alpha^3 T^4}{15 \omega_0} \Delta\alpha_0 \equiv \beta_{\text{BBR}} \left(\frac{T}{300K} \right)^4, \quad (1)$$

where T is the temperature, α is the fine structure constant, ω_0 is the unperturbed clock transition frequency, $\Delta\alpha_0$ is the difference of scalar polarizabilities of the clock states, $\Delta\alpha_0 = \alpha_0(e) - \alpha_0(g)$. The values for β_{BBR} for some known clocks as well as the ones investigated in this paper are listed in table I.

Scalar polarizability $\alpha_0(a)$ can be expressed via sums over complete sets of intermediate states involving matrix

elements of the electric dipole operator \mathbf{D} (in coordinate representation $\mathbf{D} = -e \sum_i \mathbf{r}_i = \sum_i \mathbf{d}_i$)

$$\alpha_0(a) = \frac{2}{3(2J_a+1)} \sum_n \frac{\langle a || \mathbf{D} || n \rangle^2}{E_a - E_n}. \quad (2)$$

Here $|a\rangle$ and $|n\rangle$ are many-electron atomic states and E_a and E_n are corresponding energies.

Currently the best atomic clocks have fractional accuracy level of $\Delta\omega/\omega_0 \sim 7 \times 10^{-18}$ for aluminum ion clock [2] and $\Delta\omega/\omega_0 \sim 6.4 \times 10^{-18}$ for optical lattice strontium clocks [1]. Aluminum ion clock is the only clock (operating at room temperature) where fractional BBR shift is under 10^{-17} level due to almost 98% cancellation of the clock state scalar polarizabilities [21]. The rest of the clocks require either separate measurement of BBR shift and further thermal stabilization [1, 9, 10] or cooling to cryogenic temperatures [3].

B. Quadrupole shift

Coupling of the external electric field gradient to an atomic quadrupole moment leads to the emergence of a significant systematic shift. If the electric field is aligned along quantization axis, the corresponding term in atomic Hamiltonian can be written as

$$H_Q = \frac{1}{2} Q_a \frac{\partial E_z}{\partial z}, \quad (3)$$

where Q_a is the quadrupole moment of atom, given by the following equation

$$Q_a = 2 \langle J_a J_a | E2 | J_a J_a \rangle = \langle J_a || E2 || J_a \rangle \sqrt{\frac{J_a(2J_a-1)}{(2J_a+3)(2J_a+1)(J_a+1)}}, \quad (4)$$

where J_a is the total electron angular momentum, $\langle a || E2 || a \rangle$ is the reduced matrix element of electric quadrupole transition operator. Using (3,4) one can obtain the following expression for the frequency shift between two clock states:

$$\omega = \omega_0 + (C_{J_g, M_g} Q_g - C_{J_e, M_e} Q_e) \frac{\partial E_z}{\partial z}, \quad (5)$$

where ω_0 is unperturbed transition frequency, Q_g and Q_e are ground and excited states quadrupole moments respectively, coefficients $C_{J, M}$ depend on the projection M of the total angular momentum J :

$$C_{J, M} = \frac{3M^2 - J(J+1)}{3J^2 - J(J+1)}. \quad (6)$$

Estimates for the magnitude of relative quadrupole shift in neutral and ionized erbium can be found in [8]. The values of typical electric field gradients in ion trap

$\partial E_z/\partial z \sim 10^6$ V/m² [14] that leads to the relative frequency shift for double ionized erbium is $\Delta\omega_Q/\omega_0 \sim 10^{-15}$, while for optical lattice clocks on neutral erbium these values are $\partial E_z/\partial z \sim 10^7$ V/m² [15] and $\Delta\omega_Q/\omega_0 \sim 10^{-14}$ respectively. For other atoms and ions the relative quadrupole shifts may be significantly larger and therefore require accurate treatment. There are several ways of suppression or cancellation quadrupole shift in atomic clocks. They were considered in details in [8, 16–18] and allow to achieve several orders of magnitude cancellation of quadrupole shift.

It should be pointed that if total angular momentum of an atom $F = 0, 1/2$ or total electronic angular momentum $J = 0, 1/2$ then the quadrupole momentum of corresponding state is equal to zero. Therefore it becomes sometimes possible to cancel the quadrupole shift if any of the latter conditions holds for both clock states. For most of considered elements listed in table I upper clock state has $J = 0$, therefore quadrupole shift for this states vanishes.

III. SCALAR POLARIZABILITY OF DIFFERENT LEVELS OF THE SAME CONFIGURATION.

Our numerical calculations of the polarizabilities have been performed using exact equation (2). In order to show that the scalar static polarizability has close values for levels of the same configuration it is convenient to replace summation over exact eigenstates in equation (2) by the summation over single-particle excitations from the ground state:

$$\alpha_0(a) = \frac{2}{3(2J_a + 1)} \sum_b \frac{\sum_i \langle a || \mathbf{d}_i || b \rangle^2}{E_a - E_b}, \quad (7)$$

where \mathbf{d}_i is a single electron dipole moment operator. Lets consider in details reduced matrix elements $\langle a || \mathbf{d}_i || b \rangle$. It is convenient to expand wavefunctions of the system in terms of non-relativistic configurations, so that apart from total angular momentum, the state is described by total orbital momentum L and total spin S . For simplicity lets consider two valence electron system. In total sum (7) lets separate contributions that correspond to electric dipole transition (E1) of a single electron $n_1 l_1$ to excited state $n'_1 l'_1$. In this case matrix elements in (7) can be written as

$$\langle a || \mathbf{d}_i || b \rangle = \langle n_1 l_1 n_2 l_2 L S J || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' S J' \rangle, \quad (8)$$

where operator \mathbf{d}_1 acts on 1-st electron with orbital momentum l_1 . To simplify the above expression it is convenient to use formula (13.2.5) from [27]

$$\langle n_1 l_1 n_2 l_2 L S J || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' S J' \rangle = (-1)^{J'+L+S+1} \times \Pi_{JJ'} \left\{ \begin{matrix} L' & S & L \\ J & 1 & J' \end{matrix} \right\} \langle n_1 l_1 n_2 l_2 L || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' \rangle, \quad (9)$$

where $\Pi_{JJ'} = \sqrt{(2J+1)(2J'+1)}$. Applying the same formula (13.2.5) for the orbital momentum part of wavefunction one can obtain the following expression

$$\langle n_1 l_1 n_2 l_2 L || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' \rangle = (-1)^{L'+l_1+l_2+1} \times \Pi_{LL'} \left\{ \begin{matrix} l'_1 & l_2 & l_1 \\ L & 1 & L' \end{matrix} \right\} \langle n_1 l_1 || \mathbf{d}_1 || n'_1 l'_1 \rangle. \quad (10)$$

Substituting (9), (10) in (8) one can obtain the following relation

$$\begin{aligned} & \frac{2}{3\Pi_J^2} \sum_{L',J'} \langle n_1 l_1 n_2 l_2 L S J || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' S J' \rangle^2 = \\ & \frac{2}{3} \sum_{L',J'} \Pi_{J',L',L}^2 \left\{ \begin{matrix} l'_1 & l_2 & l_1 \\ L & 1 & L' \end{matrix} \right\}^2 \left\{ \begin{matrix} L' & S & L \\ J & 1 & J' \end{matrix} \right\}^2 \times \\ & \langle n_1 l_1 || \mathbf{d}_1 || n'_1 l'_1 \rangle^2. \end{aligned} \quad (11)$$

Using formula (12.2.7) from Ref. [27] to carry out summation over J' in the above equation one gets

$$\begin{aligned} & \frac{2}{3\Pi_J^2} \sum_{L',J'} \langle n_1 l_1 n_2 l_2 L S J || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' S J' \rangle^2 = \\ & \frac{2}{3} \langle n_1 l_1 || \mathbf{d}_1 || n'_1 l'_1 \rangle^2 \sum_{L'} \Pi_{L'}^2 \left\{ \begin{matrix} l'_1 & l_2 & l_1 \\ L & 1 & L' \end{matrix} \right\}^2, \end{aligned} \quad (12)$$

and employing the same formula (12.2.7) again to sum over L' , one obtains the following equation

$$\begin{aligned} & \frac{2}{3\Pi_J^2} \sum_{L',J'} \langle n_1 l_1 n_2 l_2 L S J || \mathbf{d}_1 || n'_1 l'_1 n_2 l_2 L' S J' \rangle^2 = \\ & \frac{2}{3\Pi_{l_1}} \langle n_1 l_1 || \mathbf{d}_1 || n'_1 l'_1 \rangle^2. \end{aligned} \quad (13)$$

Summation in the above equation is over orbital momentum L' and total angular momentum J' . Energy levels $|n'_1 l'_1 n_2 l_2 L' S J' \rangle$ are assumed to be degenerate over these quantum numbers. It follows from (13) that (7) doesn't depend on L, J of state $|a \rangle$ but only on electron configuration $|n_1 l_1 n_2 l_2 \rangle$. Similar property of scalar static polarizabilities were obtained in [28] but using the assumption that the basis set is completely degenerate. In real atoms the spin-orbit interaction removes degeneracy for states with different J' of the same $^{2S+1}L'$ multiplet. For different multiplets it is removed by both the spin-orbit and the Coulomb interaction. This makes above statement about the scalar polarizabilities of all states of the same configuration to be independent on L, J to hold only approximately. In order to demonstrate this, the accurate numerical calculations of polarizabilities for tin ($5p^2$) and doubly ionized zirconium ($4d^2$) were performed. Table II presents results of calculations performed in both relativistic (the fine structure constant $\alpha = 1/137$) and non-relativistic ($\alpha \rightarrow 0$) formalisms. As one can see from table II, the statement on equality of the scalar polarizabilities for different states of the same configuration is an approximation even in the non-relativistic

TABLE II: Scalar polarizabilities for different levels of ground state configuration for tin and doubly ionized zirconium. Experimental data is taken from NIST atomic spectra database. Units for energy are inversed centimeters, polarizabilities are given in atomic units.

Z	element	config.	term	experimental energy, cm ⁻¹	calc. relativistic energy, cm ⁻¹	polarizability	calc. non-relativistic energy, cm ⁻¹	polarizability
50	Sn	5p ²	³ P ₀	0	0	50.5	0	54.7
			³ P ₁	1691.81	1720.74	52.3	0.33	54.7
			³ P ₂	3427.67	3584.07	53.7	3.12	54.7
			¹ D ₂	8612.96	9536.59	58.3	6087.3	58.5
			¹ S ₀	17162.50	18396.06	65.4	14680.56	64.5
40	Zr ²⁺	4d ²	³ F ₂	0	0	11.1	0	10.4
			³ F ₃	681.59	729.55	11.1	-2.81	10.4
			³ F ₄	1486.45	1061.73	11.1	-6.48	10.4
			¹ D ₂	5743.39	6601.21	13.6	6434.48	12.3
			³ P ₀	8063.63	8223.31	11.3	7858.93	10.7
			³ P ₁	8327.12	8504.47	11.3	7856.38	10.7
			³ P ₂	8839.97	9097.43	11.5	7853.86	10.7

TABLE III: Scalar polarizabilities of ground (J=6) and first excited (J=4) states for highly charged ions [7] sequence with configuration [Pd] 5s²4f¹² for Hf¹²⁺ and W¹⁴⁺ and [Pd] 4f¹² for rest of the atoms. $\alpha_0(g)$ and $\alpha_0(e)$ are the scalar polarizabilities of ground and first excited states respectively, their values are given in a_0^3 .

Z	element	$\alpha_0(g)$, a.u.	$\alpha_0(e)$, a.u.	$\Delta\alpha(0)/\alpha_0(g)$
72	Hf ¹²⁺	0.266690	0.267220	0.00199
74	W ¹⁴⁺	0.164300	0.164560	0.00158
76	Os ¹⁸⁺	0.110040	0.110150	0.00127
78	Pt ²⁰⁺	0.081409	0.081482	0.00090
80	Hg ²²⁺	0.062654	0.062703	0.00078
82	Pb ²⁴⁺	0.049640	0.049675	0.00071
84	Po ²⁶⁺	0.040200	0.040225	0.00062
88	Ra ³⁰⁺	0.027645	0.027660	0.00054
90	Th ³²⁺	0.023338	0.023349	0.00047
92	U ³⁴⁺	0.019886	0.019895	0.00045

approach. Although the non-relativistic solution returns exactly equal scalar polarizabilities for all states of the same multiplet, polarizabilities differ for different multiplets. Indeed, absence of the LS splitting leads to equality of energy denominators within one multiplet, so the above conclusion can be applied to the matrix elements in (7). It is interesting to note very close values of the polarizabilities of the states with the same total spin S .

Above situation significantly simplifies for highly charged ions (HCI). It corresponds to the large spin-orbit interaction case, hence states of HCI are well described in terms of jj coupling. Table III represents results of calculations of the polarizabilities for HCI with two holes in $4f$ -shell. Difference of the polarizabilities between selected components of $4f_{7/2}4f_{7/2}$ two hole states is several orders of magnitude smaller compared to the values itself. Explanation for this can be found in [20] and is similar

to the explanation presented above except that it is done in relativistic formalism. This mechanism works well for the Pa³⁺ ion considered in this work (see Table IV).

IV. RESULTS

List of suitable elements for application in ion clock and optical lattice atomic clocks is presented in Table IV. The rest of the neutral or low charged ions with two electrons or holes in opened shell have either no suitable clock transition or have Q-factors under 10^{17} . Values of the fractional BBR shifts of the clock transition frequency at room temperature are calculated using Eq. (1) and are presented in Table I. It shows that most of the considered neutral elements have BBR shift at room temperature of the same order as Ag clock [24]. Calculations were performed using the configuration interaction (CI) and the many body perturbation theory (MBPT) method. Detailed description of the method can be found in our recent papers [19, 20]. For the $4f^{12}$ opened shell configuration like in Er, Er²⁺ and Tm³⁺ we use CI calculations without MBPT [8]. The values of BBR shift at room temperature for Er, Er²⁺ and Tm³⁺ are expected to be overestimated due to the low accuracy of employed CI method for 12 and 14 valence electrons and should be considered as an upper limit.

Calculations of the quadrupole moments presented in Table IV show that a quadrupole moment of an atomic ground state can have both positive and negative sign. Indeed, sign of quadrupole moment originates from reduced matrix element in (4), which includes angular and radial integration. Although the radial part of the integral is always positive and proportional to the average squared radius of an atom, the angular integral can have both signs. Another important consequence of that explains relatively low quadrupole moments of Er, Er²⁺ and Tm³⁺ compared to the rest of the elements. Those

TABLE IV: Clock transitions in neutral atoms and low charged ions with suppressed BBR shift.

Z	element	clock states	term	calc. energy, cm ⁻¹	exp. energy, cm ⁻¹ [30, 31]	$\alpha_0(a)$, a.u.	Q_a , $ e a_0^2$	Γ , μHz	1/Q
40	Zr ²⁺	$4d^2$ $4d^2$	3F_2 3P_0	0 7902	0 8063	11.05 11.29	-0.89 0	7853	5.2×10^{-18}
40	Zr	$4d^2 5s^2$ $4d^2 5s^2$	3F_2 3P_0	0 4332	0 4196	129.8 138.6	-0.37 0	18.7	2.4×10^{-20}
52	Te	$5p^4$ $5p^4$	3P_2 3P_0	0 4736	0 4706	45.96 47.80	-2.58 0	1745	2.0×10^{-18}
53	I ⁺	$5p^4$ $5p^4$	3P_2 3P_0	0 6643	0 6447	22.08 22.48	-1.64 0	4279	3.5×10^{-18}
54	Xe ²⁺	$5p^4$ $5p^4$	3P_2 3P_0	0 8459	0 8130	14.69 14.79	-1.17 0	8756	5.7×10^{-18}
84	Po	$6p^4$ $6p^4$	3P_2 3P_0	0 7989	0 7514	54.55 59.41	-1.34 0	35709	2.5×10^{-17}
72	Hf	$5d^2 6s^2$ $5d^2 6s^2$	3F_2 3P_0	0 5172	0 5521	102.4 118.9	-0.84 0	668	6.4×10^{-19}
90	Th	$6d^2 7s^2$ $6d^2 7s^2$	3F_2 3P_0	0 2187	0 2558	163 165.7	-1.23 0	22.3	4.6×10^{-20}
68	Er	$4f^{12} 6s^2$ $4f^{12} 6s^2$	3H_6 3F_4	0 6169	0 5035	150.2 150.2	0.71 -0.01	25.1	2.6×10^{-20}
91	Pa ³⁺	$5f^2$ $5f^2$	3H_4 3F_2	0 3329	0 2878	9.86 10.07	-1.12 0.30	19.6	3.6×10^{-20}
91	Pa ³⁺	$5f^2$ $5f^2$	3F_2 3P_0	3329 12989	2878 11512	10.07 10.67	0.30 0	3467	2.1×10^{-18}
68	Er ²⁺	$4f^{12}$ $4f^{12}$	3H_6 3F_4	0 6159	0 5081	3.91 2.80	0.40 -0.02	8.4	8.7×10^{-21}
69	Tm ³⁺	$4f^{12}$ $4f^{12}$	3H_6 3F_4	0 6714	0 5640	0.85 0.80	0.30 -0.01	8.6	8.1×10^{-21}
71	Lu ⁺	$6s^2$ $5d 6s$	1S_0 3D_1	0 11995	0 11796	63.10 60.87	0 0	12.2	4.2×10^{-21}

elements acquire their quadrupole momenta due to presence of two holes in $4f$ -shell. Average squared radius of $4f$ -shell is significantly smaller than the ones of $6s$, $6p$, $5d$ -shells and is of the same order of magnitude as the one of $4d$ -shell. Indeed, the quadrupole moment of zirconium ground state is only two times smaller than the one of erbium. Therefore, extrapolating to the rest of lanthanides and actinides with configurations $(n-2)f^N ns^2$ or $(n-2)f^N$ one can expect them to have relatively small quadrupole momenta.

As it was pointed in the end of section II B, the clock states with either total angular momentum of an atom $F = 0, 1/2$ or total electronic angular momentum $J = 0, 1/2$ have no quadrupole shift. Selection of the following isotopes ^{91}Zr ($I = 5/2$), ^{127}I ($I = 5/2$), ^{131}Xe ($I = 3/2$), ^{231}Pa ($I = 3/2$) would result in emerging of the hyperfine component of the ground state with $F = 1/2$, while the first excited state for considered neutral atoms and ions of these elements will have electronic angular momentum $J = 0$ (the second excited state for $^{231}\text{Pa}^{3+}$). Therefore, it is possible to completely cancel quadrupole shift for

proposed clock transitions in ^{91}Zr , $^{91}\text{Zr}^+$, $^{127}\text{I}^+$, $^{131}\text{Xe}^{2+}$, and $^3F_2 \rightarrow ^3P_0$ in $^{231}\text{Pa}^{3+}$.

It should be noted that presented elements were chosen only due to the presence of a clock transition between different states of the same configuration. This guarantees cancellation of BBR shift of no less than one order of magnitude. However, the 98% cancellation of BBR shift in aluminum ion clock occurs between levels of different configurations. Calculations for Lu^+ shows similar two orders of magnitude cancellation for the strongly forbidden M1 transition. Therefore, neutral atoms and low charged ions considered in this paper can only be a part of the full list of elements suitable for ultra-precise atomic clocks with suppressed BBR shift.

V. DISCUSSION OF ACCURACY

For calculations of the polarizabilities we employed the CI+MBPT method [19, 20] for all elements except Er^{2+} and Tm^{3+} for which CI for many-valence-electron

TABLE V: Energies and transition amplitudes of odd levels that contribute to polarizability of neutral thorium $[\text{Rn}]6d^27s^2$ ground state. This table displays only several levels with energies under 20000 cm^{-1} .

leading configuration	total momentum	energy, cm^{-1}		transition amplitude, a.u.
		[31]	our calculation	
$5f6d7s^2$	2	8243	9671	-0.0852
$5f6d7s^2$	3	10526	12222	0.4618
$6d7s^27p$	2	10783	10452	0.1345
$5f6d7s^2$	3	11241	13664	-0.3952
$6d7s^27p$	1	11877	13204	0.3928
$5f6d7s^2$	2	12114	15147	0.5077
$6d7s^27p$	3	13945	13875	0.5466
$6d7s^27p$	2	14032	15357	0.1334
$5f6d7s^2$	1	14243	17155	0.3326
$6d^27s7p$	2	14465	13647	0.5827
$5f6d^27s$	3	15618	14484	0.1534
$6d^27s7p$	1	15736	15944	0.9344
$6d7s^27p$	2	16217	17707	-0.1304
$6d^27s7p$	2	17224	16608	-0.4105
$5f6d7s^2$	1	17354	17511	0.5506
$6d7s^27p$	3	17411	16260	0.1057
$5f6d7s^2$	2	17847	19116	-0.1011
$6d7s^27p$	3	18069	18270	-0.3416
$6d^27s7p$	1	18614	18271	-0.2221
$6d^27s7p$	3	18930	19000	-0.0687
$6d^27s7p$	3	19503	18638	-0.4439
$6d^27s7p$	2	19516	19401	0.1840
$6d^27s7p$	1	19817	21020	-0.7016
$6d^27s7p$	3	20423	21248	0.4502
$6d7s^27p$	1	20423	21796	-0.0428
$6d^27s7p$	2	20522	19763	-0.1900

systems was used [8]. The accuracy of the CI+MBPT method depends on the number of valence electrons. Better than 3% accuracy can be achieved for two valence electron systems while for four electrons the uncertainty is larger and can reach 6%. It should be mentioned that in [20] the CI+MBPT method was employed for lanthanides and actinides with up to 16 electrons in open shells. In this paper we used the same approach for Er. It was possible due to the separation of the f -shell valence electrons from the s -, p - and d -shell ones and attributing them to the core (see [20] for details). This allowed to reduce the many electron problem to 2-3 valence electrons. Estimated accuracy of this approach for calculation of polarizabilities of lanthanides and actinides was 13%. One may argue that this accuracy is not sufficiently high to claim strong cancellation of the polarizability values. However, since we consider similar states and perform identical calculations for both states we expect strong cancellations of the uncertainties similar to the cancellations of the polarizabilities.

The Zr, Hf, and Th atoms require separate consideration due to larger number of valence electrons. Each of these atoms have four valence electrons and accurate treatment of the interactions between them leads to a

very large configuration interaction matrix which is beyond our present computational capabilities. Presented results were obtained by using smaller number of allowed excitations compared to other atoms. Such cut of the CI basis set led to some reduction of accuracy. We estimate it on the level of 6% compared to 3% accuracy for atoms with two or three valence electrons.

Comparing our result for Zr, Hf and Th with the ones in [29, 30] one can notice good agreement for Zr and Hf and some disagreement for Th. We have no explanation for this disagreement. We stress that we perform very similar calculations for all three atoms, have similar accuracy for the energies and expect similar accuracy for the polarizabilities. Table V presents some results of our calculations for energies and transition amplitudes for levels of odd parity with $J = 1, 2, 3$ in interval of up to 20000 cm^{-1} that contribute to the scalar polarizability of the thorium ground state.

For Er^{2+} and Tm^{3+} ions, which have only f valence electrons, the calculations were performed using the many-electron version of the CI method [8] which has accuracy of about 20%. Note that absence of s or p valence electrons leads to small values of the polarizabilities and small difference between polarizabilities of the

ground and clock states. Therefore, high accuracy of the calculations is less important for such systems.

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